

PHOTO-OXIDATIVE DEGRADATION OF AZO DYES ON TRANSITION METAL OXIDE ELECTRODES

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Degradation of organic pollutants by means of semiconductor photocatalysis has been extensively investigated. Studies of the degradation of textile azo dye pollutants on colloidal suspensions of TiO_2 semiconductor nanoparticles have been reported by Kamat and coworkers [1,2]. In our previous studies [3], we have employed a photoelectrocatalytic system, with nanoparticulate TiO_2 and WO_3 film electrodes, for degradation of organic pollutants. The photoelectrocatalytic route was subsequently applied in studies of mineralization of methylene blue dye. In this work, we have investigated the degradation processes of textile azo dyes: Naphthol Blue Black (NBB), Chicago Sky Blue (CSB), Orange II, and others, using a photoelectrocatalytic route. The advantages of the photoelectrochemical method lie in the separation of the semiconductor catalyst particles from the solution and direct control of the interfacial potential. We have found the photoelectrochemical method to be an efficient and convenient method of degrading organic dyes.

We have investigated the performance of three different photoelectrocatalytic materials, based on the transition metal oxides: TiO_2 , WO_3 , and MoO_3 . These self-doped nonstoichiometric compound semiconductors were of n -type with specific conductance guaranteeing a negligible ohmic potential drop across the thin semiconductor film on Pt substrate used as the working electrode. We have found the performance of WO_3 film electrodes to be the best in most cases. Although the subtle differences in the real active surface area and surface morphology may also play some role, we believe that the main reason for the best performance of WO_3 lies in the location of the valence band edge E_{VB} . Among the semiconductors investigated, WO_3 has the highest E_{VB} , thus providing electron holes with the highest energy. By annealing the nanoparticulate WO_3 films deposited on a Pt substrate, we were able to further increase the photodegradation rates of dyes, owing to the reduction of losses due to electron-hole recombination.

The photoelectrochemical degradation rates measured at different potentials were compared with photocurrents generated at nanoparticulate semiconductor film electrodes. The results obtained indicate that the degradation rate is proportional to the photocurrent.

The degradation rates for mono-azo dyes, such as the Orange II, were considerably higher than those for di-azo dyes, represented by CSB and NBB. The rate constants k were evaluated from the linear plots of $1/v$ vs. $1/C_0$, which is based on generally accepted Langmuir-Hinshelwood mechanism (v is the reaction rate and C_0 is the initial dye concentration). For instance, for NBB the values of k ranged from $0.62 \times 10^4 \text{ M}^{-1}$ to $2.34 \times 10^4 \text{ M}^{-1}$, depending on the illumination intensity. Lower k values were obtained for CSB. The effect of initial concentration of dyes on the degradation rate was also investigated.

The photoelectrocatalytic degradation of dyes also occurs under illumination with visible light, however, in this case it is significantly slower than that observed under UV illumination.

The mechanism of reactions taking place during the photodegradation process is proposed. It is based on two routes: (i) the main path, involving electron-hole generation and heterogeneous oxidation with participation of valence band holes, and (ii) the side path, involving dye self-sensitization and sub-band excitation under visible light illumination. The main route reactions involve oxidation of solution components with generation of powerful radical oxidants, being directly responsible for the fast dye decomposition. The reaction intermediates and final degradation products were evaluated using HPLC technique.

References

1. K. Vinodgopal and P. Kamat, *Environmental Science & Technology*, **29** (1995) 3.
2. K. Vinodgopal, I. Bedja, S. Hotchandani, and P. Kamat, *Langmuir*, **10** (1991) 6.
3. M. Hepel and J. Luo, *Electrochim. Acta* (in press).